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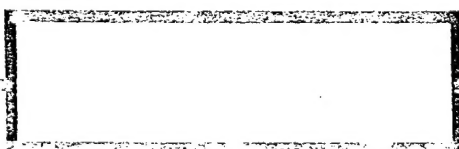
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HIGH-TEMPERATURE ANNEALING PROPERTIES OF SiGe/GaP ALLOYS

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University of Wales, College of Cardiff, U. K.

[Absract] As discovered in annealing studies with SiGe/GaP
alloys, further improvements are attained in the thermoelectric
power factor (alpha^2.sigma) of the material after three-step
annealing (high temperature-low temperature-high temperature) of
this alloy.

Key Words: SiGe alloys, high-temperature annealing,
thermoelectric properties.

i. Introduction

As a matured semiconductor thermoelectric power generation
material, SiGe alloy is suitable in the manufacture of
radioactive isotope thermoelectric power generators; on several
occasions, the alloy is used in building power supply systems for
satellites and space probes [1]. However, efforts are still
going on to further improve the properties of such materials. As
is well known, an important parameter in evaluating the
performance of thermoelectric materials is the optimum value

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: alpha is the Seebeck coefficient; epsilon is electroconductivity; and lambda is thermal conductivity. In the past, for a very long time the principal research was aimed at upgrading the material's optimal value by reducing the thermal conductivity of the crystal lattice. Theoretically speaking, the short-range randomness can be introduced in the material structure, forming effective scattering centers of shorter-wavelength phonons. However, there is no obvious scattering function for longer-wavelength carriers. Therefore, when electroconductivity is not reduced, the optimal value of the material can be upgraded by decreasing the thermal conductivity of the crystal lattice. Rowe et al. of the University of Wales, U.K., applied a powder metallurgical method to prepare a fine-crystalline SiGe alloy; thus, the lattice thermal conductivity is 28% lower [2]. Pisharady of Syncal Corporation in the United States doped GaP in an SiGe alloy to also appreciably decrease the lattice thermal conductivity of the material [3]. Unfortunately, however, in the two above-mentioned occasions, the reduction in thermal conductivity was also accompanied by a reduction in electroconductivity. Therefore, the optimal value of the material was not really improved.

Not long ago, as reported by Vandersande et al of the Jet Propulsion Laboratory in California, United States, the thermoelectrical optimal value was appreciably improved by high-temperature annealing (1200-1275°C) of GaP-doped SiGe alloy. The main cause of this improvement was due to a marked reduction in

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the resistivity after annealing, but the Seebeck coefficient and thermoelectricity only decreased slightly. As predicted by further research, this was because of higher solid-state solubility of the dopant elements in the alloys [4]. As pointed out by theoretical estimates (Bhandari and Rowe), the contribution made by improving material performance with greater solid-state solubility of the dopant elements was only about half of the experimental values; other regimes possibly exist. After high-temperature annealing, this other possible regimes may also contribute to improving the thermoelectric properties.

II. Experiments

The specimens used in the experiments were supplied by the Jet Propulsion Laboratory in California, the United States. These specimens included polycrystalline n-type SiGe/GaP alloy made by the powder metallurgy method. Specimen G1 was cut from a circular wafer material with density $2.95 g/cm^3$, with dimensions 2.01x2.17x3.90mm. With X-ray diffraction analysis, the constituents of the material were found to be $Si_{0.85}Ge_{0.15}$. The specimen underwent a series of annealings in the following sequence: $1200^{\circ}C$, $1100^{\circ}C$, $1000^{\circ}C$, $900^{\circ}C$, $800^{\circ}C$, and $1200^{\circ}C$. The annealings were conducted in the atmosphere; each annealing lasted 2h. The Seebeck coefficient and resistivity of the material were measured after each annealing, in the range $25-550^{\circ}C$. Refer to [5] in the references for the annealing and measurement systems used. The average of measurements in two

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tests was used for greater precision of measurement. Besides, to avoid possibly present surface defects, washing, cleaning, and slight grinding-polishing of the specimen were conducted as required before measurements [6].

Specimens G3 and G4 were cut (and processed) from adjacent positions of the same circular wafer with density $2.90g/cm^3$ in order to ensure that the thermoelectric properties of the two specimens are identical to the greatest extent. The dimensions of the specimens were, respectively, 2.20x2.59x5.85mm and 1.97x2.75x6.25mm. These two specimens were used to prove the results obtained after the annealing sequence: high temperature-low temperature-high temperature. Therefore, specimen G1 was subjected to three annealing treatments: 1200, 700, 1200$^{\rm o}$C; each annealing period was 2h, for a total of 6h. The specimen G underwent a continuous annealing for 6h at 1200$^{\rm o}$C.

III. Experimental Results and Discussion

Figs. 1(a), (b), and (c) present the variations of the Seebeck coefficient, resistivity, and thermoelectric power factor with temperature, for specimen G1 before and after annealing. For sake of clearer diagrams, the results of annealing at 1000 and 900$^{\rm o}$C are not included. However, the results of variation of the three parameters with temperature are the same as the results for annealing at 800.$^{\rm o}$C. From the figure, after the first annealing (1200$^{\rm o}$C, 2h) of the specimen, its resistivity decreased appreciably; however, its Seebeck coefficient was only slightly
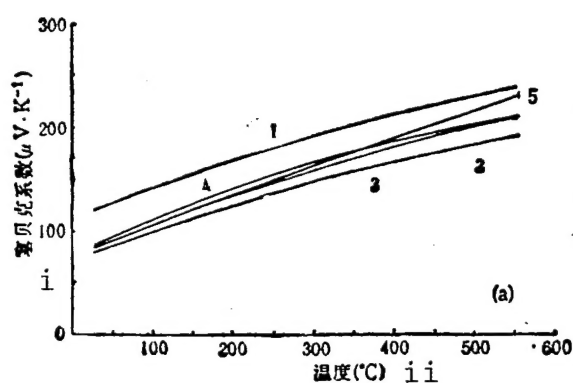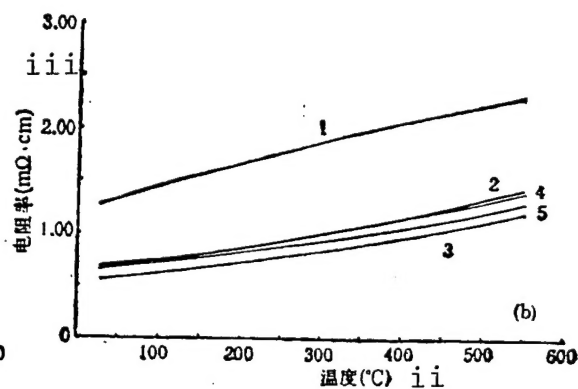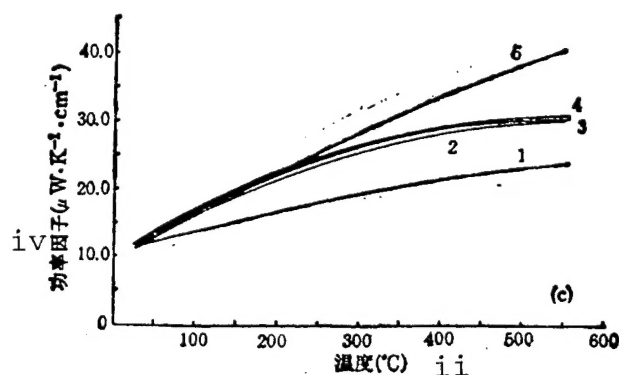
Fig. 1: (a) Variation in Seebeck coefficient with temperature (specimen G₁)

(b) Variation of resistivity with temperature (specimen G1)

(c) Variation in power factor with temperature (specimen G¹)

LEGEND: 1 - before annealing   2 - annealing 1 (1200 °C, 2h)
          3 - annealing 2 (1100 °C, 2h)   4 - annealing 5
          (800 °C, 2h)   5 - annealing 6 (1100 °C, 2h)

KEY: i - Seebeck coefficient   ii - temperature
iii - resistivity   iv - power factor

less. This is due to the significant reduction in resistivity greatly exceeding the amount of reduction for the Seebeck coefficient; therefore, the thermoelectric power factor of the

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material was increased. This outcome supports the results made
by Vandersande et al. From the trend in variation of the Seebeck
coefficient and resistivity before and after annealing, the
reason was possibly due to the increase in carrier concentration
in the material. In other words, the solid-state solubility of
the dopant elements was increased after high-temperature
annealing of SiGe/GaP alloy.

After the second annealing (1100°C, 2h) for the specimen,
its Seebeck coefficient and resistivity further slightly
decreased; however, its power factor $\alpha^2\sigma$ decreased slightly.
Consequently, after three low-temperature annealings (1000°C,
900°C, 800°C, 2h each) its power factor showed almost no change.
However, the Seebeck coefficient and resistivity rose somewhat
compared to their values after higher-temperature annealing. In
other words, lower-temperature annealing resulted in reversing
the variational trend of the Seebeck coefficient and resistivity.

If another higher-temperature annealing (1100°C, 2h) was
conducted with the specimen, its power factor was further
improved. As shown in Fig. 1(c), this improvement occurred after
the measured temperature exceeded 300°C; the power factor
increases with higher temperature. Noteworthy is the fact that
the cause of the continued rise in the thermoelectric power
factor was that resistivity slightly increases after annealing,
but the Seebeck coefficient rose. This trend in variation
obviously is difficult to explain with increasing carrier
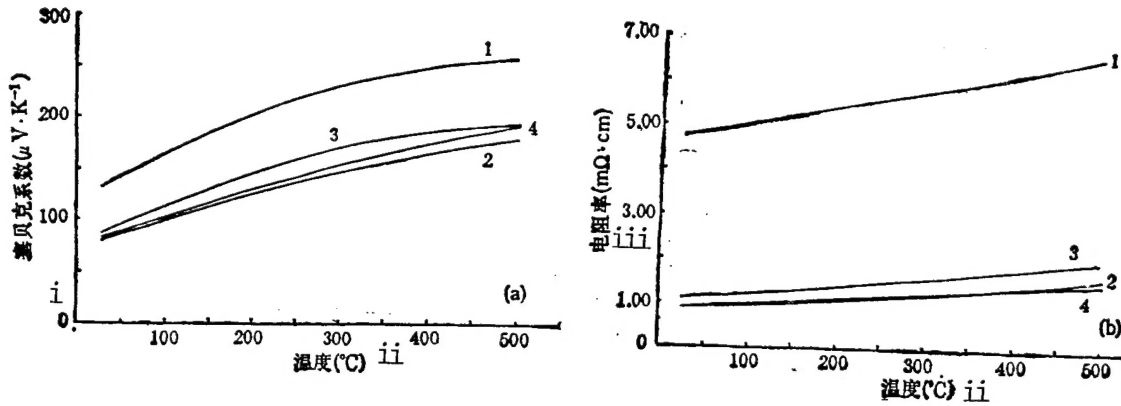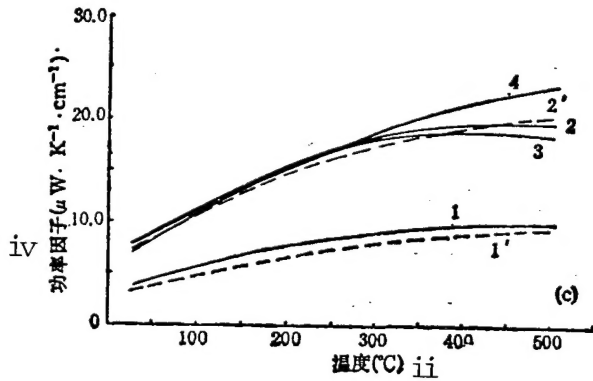concentration.

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Fig. 2. (a) Variation in Seebeck coefficient with temperature (specimen G3)

(b) variation of resistivity with temperature (specimen G 3)

(c) Variation in power factor with temperature (specimens G 3 and G 4)

LEGEND: 1 - before annealing for specimen G3 2 - specimen G3, annealing 1 (1200 °C, 2 h) 3 - specimen G 3, annealing 2 (700 °C, 2h) 4 - specimen G 3, annealing 3 (1200 °C, 2h): 1' - before annealing for specimen G 4, 2' - after annealing for specimen G 4 (1400 °C, 6h)

KEY: i - Seebeck coefficient ii - temperature iii - resistivity iv - power factor

Fig. 2(a) and (b) show the trends in variation with temperature for the Seebeck coefficient and for resistivity after

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the three-step annealing of specimen G3. Fig. 2(c) shows the variation with temperature for the power factor in the case of specimens G3 and G4. From the above-mentioned experimental results, the following conclusions may be drawn: first, the results obtained after the three-step annealing (high temperature-low temperature-high temperature) of specimen G1 were proved. In other words, the power factor of the material showed a further improvement. Second, this three-step annealing shows a better improvement in the power factor compared with single-step high-temperature annealing for the same annealing period. By comparing specimens G1 and G3, it is also shown that whatever the large differences of the thermoelectric properties, mass and density values of both specimens before annealing, still after three-step annealing the trends in variation with temperature for the Seebeck coefficient and the resistivity are basically consistent. This appears to suggest that the first high-temperature annealing improves the thermoelectric power factor of the material; the principal reason was due to increasing solid-state solubility of the dopant elements in the alloy. However, after a further three-step annealing, the resistivity showed a lowering trend with temperature, but the Seebeck coefficient showed a rising trend with increase in temperature; the trend is more apparent as the temperature is higher. This trend apparently contributes to improving the thermoelectric properties of the material. Actually, after the specimen was subjected to the third step of high-temperature annealing, the relative change

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with temperature for the Seebeck coefficient and for resistivity was more important than their numerical variation. This result helps in making the prediction that other regimes also contribute to improving the thermoelectric power factor. For example, the temperature-dependent relationships of the Seebeck coefficient and resistivity are very sensitive to change in the scattering mechanism.

IV. Conclusions

After high-temperature annealing of the SiGe/GaP alloy, its thermoelectric power factor can be clearly increased. This improvement is possibly due to greater solid-state solubility of the dopant elements in the alloy. However, when the alloy goes through three-step annealing (high temperature-low temperature-high temperature), the thermoelectric power factor of the material can be further increased. However, this increase cannot be explained by the rise in the solid-state solubility of the dopant elements in the alloy. This shows that other regimes make contributions to the improvement in the thermoelectric power factor that cannot be neglected. Moreover, this hints that this three-step annealing may also be used in annealing treatment of other thermoelectric materials.

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